

- please answer all 5 questions in the spaces provided
- this is a 2-hour test
- a calculator and the equation sheets provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

1. This question refers to the cell $\text{Pt(s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{HCl}(\text{aq}, 0.100 \text{ mol kg}^{-1}) | \text{AgCl(s)} | \text{Ag(s)} | \text{Pt(s)}$.

The cell reaction is $\text{H}_2(\text{g}) + 2\text{AgCl(s)} = 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Ag(s)}$.

- a) Write the Nernst equation for the cell.
- $$E = E^\circ - \frac{RT}{nF} \ln Q$$
- $$Q = \frac{a_{\text{H}^+(\text{aq})}^2 a_{\text{Cl}^-(\text{aq})}^2 a_{\text{Ag(s)}}^2}{a_{\text{H}_2(\text{g})} a_{\text{AgCl(s)}}^2} = \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 (1)^2}{P_{\text{H}_2} (1)^2}$$
- $$E = E^\circ - \frac{RT}{2F} \ln \left(\frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{P_{\text{H}_2}} \right)$$

- b) Assuming the aqueous hydrochloric acid solution is ideal, calculate the cell voltage (E) at 25 °C.

Data: $E^\circ = 0.2221 \text{ V}$.

$$\left. \begin{array}{l} \delta_+ = 1 \rightarrow a_{\text{H}^+} = \delta_+ m_{\text{H}^+} = m_{\text{H}^+} \\ \delta_- = 1 \rightarrow a_{\text{Cl}^-} = \delta_- m_{\text{Cl}^-} = m_{\text{Cl}^-} \end{array} \right\} \text{for ideal solutions}$$

$$E = E^\circ - \frac{RT}{2F} \ln \left[\frac{(0.100)^2 (0.100)^2}{1} \right]$$

$$= 0.2221 \text{ V} - \frac{8.314 (298.15)}{2 (96485)} \ln(0.100^4)$$

$$= 0.2221 \text{ V} + 0.1183 \text{ V}$$

$$E = 0.3404 \text{ V}$$

- c) Explain how the cell could be modified to measure partial pressures of hydrogen gas.

$$E(P_{\text{H}_2}) - E(P_{\text{H}_2} = 1 \text{ bar}) = -\frac{RT}{2F} \ln \left(\frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{P_{\text{H}_2}} \right) - \left[-\frac{RT}{2F} \ln \left(\frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{1 \text{ bar}} \right) \right]$$

$$= \frac{RT}{2F} \ln(P_{\text{H}_2}) \quad \text{a } P_{\text{H}_2} \text{ meter!} \quad \text{cell voltage changes with } P_{\text{H}_2}$$

- d) Explain how the cell could be modified to produce silver from silver chloride.

Problem: H^+ , Cl^- ion concentrations will build up in the cell, making the reaction nonspontaneous

Suggestion: pump out H^+ , Cl^- reaction products, pump in fresh water (and keep adding H_2 and AgCl)

2. The probability distribution function for molecular velocities v_x is

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2kT}\right)$$

a) The Boltzmann distribution, a fundamental law of nature, states that the probability a molecule has energy E_i is proportional to $\exp(-E_i/kT)$. Explain how $f(v_x)$ illustrates the Boltzmann distribution.

kinetic energy of a molecule of mass $m = \frac{1}{2} m v_x^2$

$$\exp\left(-\frac{mv_x^2}{2kT}\right) = \exp\left(-\frac{\frac{1}{2} m v_x^2}{kT}\right) = \exp\left(-\frac{\text{energy}}{kT}\right)$$

b) Give the numerical value of the following integrals:

- i) $\int_{-\infty}^{\infty} f(v_x) dv_x = \boxed{1}$ $f(v_x)$ is normalized
- ii) $\int_0^{\infty} f(v_x) dv_x = \boxed{\frac{1}{2}}$ $\frac{1}{2}$ of the molecules move in the positive x -direction
- iii) $\int_{-\infty}^{\infty} v_x f(v_x) dv_x = \langle v_x \rangle = \boxed{0}$ positive ($v_x > 0$) and negative ($v_x < 0$) velocities equally probable

c) Use the definite integral $\int_0^{\infty} u e^{-au^2} du = \frac{1}{2a}$ to prove $\int_0^{\infty} v_x f(v_x) dv = \sqrt{\frac{kT}{2\pi m}}$.

$$\begin{aligned} LS &= \int_0^{\infty} v_x f(v_x) dx \\ &= \int_0^{\infty} v_x \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x \quad \left(a = \frac{m}{2kT}\right) \\ &= \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^{\infty} v_x e^{-mv_x^2/2kT} dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^{\infty} v_x e^{-av_x^2} dv_x \\ &= \left(\frac{m}{2\pi kT}\right)^{1/2} \frac{1}{2a} = \left(\frac{m}{2\pi kT}\right)^{1/2} \frac{1}{2\left(\frac{m}{2kT}\right)} \\ &= \left(\frac{kT}{2\pi m}\right)^{1/2} \\ &= RS \end{aligned}$$

3. a) The previous question shows that the average velocity of molecules in a given direction is $\langle v \rangle / 4$. This result is very useful for understanding rates of effusion, wall collisions, diffusion, heat conduction and many other processes. Why?

$$c \int_0^{\infty} v_x f(v_x) dx = c \langle v \rangle / 4 \text{ gives the average number}$$

of molecules moving in a given direction to:

collide with a wall, leak through a hole, transport mass or heat etc.

- b) ${}^7\text{Li}$ vapor (7.02 g mol^{-1}) at 7215 Pa and 775°C leaks out of a Knudsen cell into a vacuum chamber through a 0.25 mm diameter hole. Calculate the number of grams of ${}^7\text{Li}$ lost from the cell per hour.

$$\text{hole area } A = \pi r^2 = \pi \left(\frac{0.00025 \text{ m}}{2} \right)^2 = 4.91 \times 10^{-8} \text{ m}^2$$

$$\text{leak rate per unit area } Z_c = \frac{P}{\sqrt{2\pi m k T}}$$

$$Z_c = \frac{7215 \text{ Pa}}{\sqrt{2\pi (0.00702 \frac{\text{kg}}{\text{mol}}) \left(\frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) (1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}) (1048 \text{ K})}}$$

$$Z_c = 2.22 \times 10^{26} \text{ } {}^7\text{Li atoms m}^{-2} \text{ s}^{-1}$$

$$\text{leak rate through hole} = Z_c A$$

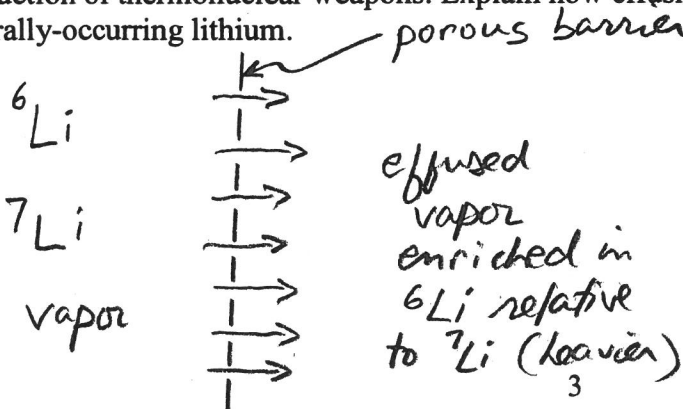
$$Z_c A = (2.22 \times 10^{26} \text{ Li atoms m}^{-2} \text{ s}^{-1}) (4.91 \times 10^{-8} \text{ m}^2)$$

$$= 1.09 \times 10^{19} \text{ Li atoms per second}$$

$$= (1.09 \times 10^{19} \text{ Li atoms s}^{-1}) \left(3600 \frac{\text{s}}{\text{hr}} \right) = 3.92 \times 10^{22} \frac{\text{atoms}}{\text{hr}}$$

$$= \left(3.92 \times 10^{22} \frac{\text{atoms}}{\text{hr}} \right) \left(\frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) \left(7.02 \frac{\text{g}}{\text{mol}} \right) = \boxed{0.456 \frac{\text{g}}{\text{hr}}}$$

- c) Naturally-occurring lithium is a mixture ${}^6\text{Li}$ and ${}^7\text{Li}$. The ${}^6\text{Li}$ isotope is extremely valuable for the production of thermonuclear weapons. Explain how effusion can be used to obtain pure ${}^6\text{Li}$ from naturally-occurring lithium.



$$\text{effusion rate} \propto \frac{1}{\sqrt{m}}$$

take effused vapor, effuse it again (further ${}^6\text{Li}$ enrichment) repeat, ...

4. a) For O_2 molecules (32.0 g mol^{-1} , $\sigma = 0.409 \text{ nm}^2$) at 300 K and 1.00 bar calculate:

i) the average speed $\langle v \rangle$

$$\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{\pi (0.0320 \text{ kg mol}^{-1})}}$$

$$= \boxed{446 \text{ m s}^{-1}}$$

ii) the mean free path λ

$$\lambda = \frac{kT}{\sqrt{2} p \sigma} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{\sqrt{2} (10^5 \text{ Pa})(0.409 \times 10^{-18} \text{ m}^2)}$$

$$= \boxed{7.16 \times 10^{-8} \text{ m}} \quad (71.6 \text{ nm})$$

iii) the diffusion coefficient (use $D = \lambda \langle v \rangle / 2$)

$$D = \frac{\lambda \langle v \rangle}{2} = \frac{(7.16 \times 10^{-8} \text{ m})(446 \text{ m s}^{-1})}{2}$$

$$= \boxed{1.60 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}}$$

iv) the rms displacement of diffusing O_2 molecules after diffusion for 1 second

$$\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

$$= \sqrt{2(1.60 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})(1 \text{ s})}$$

$$= \boxed{0.00565 \text{ m}} \quad (0.565 \text{ cm})$$

b) Part a shows that molecules with speeds of hundreds of meters per second diffuse only a fraction of a centimeter per second! Why is diffusion so slow?

Molecules moving at hundreds of meters per second travel only microscopic distances ($\lambda \approx 100 \text{ nm}$) before colliding with other molecules and bouncing in random directions, including "backwards" or "sideways", making little progress in any direction.

5. a) We used kinetic theory to derive $D = \lambda \langle v \rangle / 2$. The random-walk model for a molecule taking steps of length λ every τ seconds appears to give a different result: $D = \lambda^2 / 2\tau$.

In fact, these two equations for the diffusion coefficient are identical! Show

$$\lambda \langle v \rangle / 2 = \lambda^2 / 2\tau$$

Hint: The average speed equals the mean free path divided by the average time between collisions. ($\langle v \rangle = \frac{\lambda}{\tau}$)

$$\begin{aligned} RS &= \frac{\lambda^2}{2\tau} \\ &= \lambda \frac{\lambda}{\tau} \frac{1}{2} \\ &= \frac{\lambda \langle v \rangle}{2} \end{aligned}$$

$$\left(\begin{aligned} \text{or: } RS &= \frac{\lambda^2}{2\tau} = \frac{\lambda^2}{2 \frac{1}{z_{11}}} = \frac{\lambda^2 z_{11}}{2} \\ &= \frac{1}{2} \left(\frac{1}{(N/V) \sqrt{2} \sigma} \right)^2 \left(\frac{N}{V} \sqrt{2} \sigma \langle v \rangle \right) \\ &= \frac{1}{2} \frac{\langle v \rangle}{(N/V) \sigma \sqrt{2}} = \frac{1}{2} \lambda \langle v \rangle \end{aligned} \right)$$

- b) A window consists of a sheet of glass 4.00 m wide, 3.00 m high and 1.00 cm thick. Calculate the heat flow through the window on a winter day if the inside temperature is 22 °C and the outside temperature is -10 °C. Give your answer in units of J s⁻¹.

Data: the thermal conductivity of the window glass is $\kappa = 0.80 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$

heat flux $J_x = -\kappa \frac{\partial T}{\partial x} = -\kappa \frac{\Delta T}{\Delta x}$

$$J_x = - \left(0.80 \frac{\text{J}}{\text{m K s}} \right) \frac{-10^\circ\text{C} - 22^\circ\text{C}}{0.0100 \text{ m}} = \frac{0.80(32)}{0.0100} \frac{\text{J}}{\text{m}^2 \text{ s}}$$

$$J_x = 2560 \text{ J m}^{-2} \text{ s}^{-1} \text{ (per unit area)}$$

heat flow through the glass $= J_x A = \left(256 \frac{\text{J}}{\text{m}^2 \text{ s}} \right) (12.0 \text{ m}^2)$

$$= \boxed{30720 \frac{\text{J}}{\text{s}}}$$

- c) The windows in many modern buildings consist of two parallel sheets of glass separated by a thin air-filled gap. Why are two panes of glass used?



air gap acts as an insulating layer
 ($\kappa_{\text{air}} \ll \kappa_{\text{glass}}$)
 reducing heat loss in the winter
 (and heat gain from outside in summer)

Q1
 Q2
 Q3
 Q4
 Q5